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NO DRAWINGS

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(45) COATING COMPOSITIONS

(71) We, E. I. DU PONT DE NEMOURS & COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to tetrafluoroethylene polymer aqueous dispersions used for coating purposes, and more particularly to such dispersions which provide coatings of improved gloss.

The properties of non-melt-fabricable tetrafluoroethylene polymers such as high temperature resistance, chemical stability, and low friction surface, have led to the widespread use of these polymers in the form of films, coatings and impregnants. Unfortunately, the nature of the polymer, i.e. the fact that it is sintered rather than melt-fabricated, causes the exposed surface of the polymer to have some degree of roughness which, in turn, renders the surface not as glossy as desired for some applications for aesthetic or for functional reasons.

It has now been found that the gloss of coatings obtained from aqueous dispersions of a non-melt-fabricable tetrafluoroethylene copolymer can be improved by incorporating into the dispersion a small, gloss improving, amount of a dispersion of a melt-fabricable tetrafluoroethylene copolymer and a nonionic surfactant. Accordingly the present invention provide a coating composition which comprises an aqueous dispersion of:

- (a) a non-melt-fabricable (as hereinafter defined) tetrafluoroethylene polymer,
(b) 1 to 6% by weight, based on the weight of (a), of a melt-fabricable (as hereinafter defined) tetrafluoroethylene copolymer, and
containing, dissolved therein, a non-ionic surfactant.

The resultant aqueous dispersion when cast in a conventional manner such as by contacting a substrate and the dispersion, followed by drying the dispersion and sintering the tetrafluoroethylene polymer (a), yields a tetrafluoroethylene polymer coating of improved gloss over that which is obtained for the current commercially available tetrafluoroethylene polymer dispersions.

Each component of compositions of the present invention, i.e. the non-melt-fabricable tetrafluoroethylene polymer (a) (as aqueous dispersion), the melt-fabricable tetrafluoroethylene copolymers (b) (as aqueous dispersion), and the surfactant, is a well-known material of commerce. More specifically, the non-melt fabricable tetrafluoroethylene polymer component can be obtained as a dispersion of colloidal particles of non-melt-fabricable tetrafluoroethylene polymer in water. Examples of such dispersions include those disclosed in U.S. Patent Specifications Nos. 2,534,058, (Renfrew), 2,559,752, (Berry), and 2,559,749, (Benning), as well as the concentrated tetrafluoroethylene polymer aqueous dispersions disclosed in U.S. Patent Specifications Nos. 2,478,229, (Berry) and 3,037,953 (Marks and Whipple), and the large particle dispersions disclosed in U.S. Patent Specification No. 3,391,099 (Punderson). The tetrafluoroethylene polymer in the aqueous dispersion can be a homopolymer or a copolymer of tetrafluoroethylene with a small amount of another copolymerizable monomer, such as up to two percent by weight of units derived from perfluoroalkyl ethylene or oxyperfluoroalkyl trifluoroethylene of 3 to 10 carbon atoms, as disclosed in U.S. Patent Specification No. 3,142,665, (Cardinal, Edens, and Van Dyk). The preferred comono-

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mer is hexafluoropropylene. The resultant tetrafluoroethylene polymer must retain its non-melt-fabricable character.

5 Briefly, a process for making the dispersion generally involves introducing tetra-
fluoroethylene under pressure into an aqueous solution of a polymerization initiator
and a dispersing agent under mild agitation to produce an aqueous dispersion of
colloidal size particles of tetrafluoroethylene polymer in concentrations of 15 to 45
percent by weight of polymer solids. The present invention does not depend on which
polymerization initiator and dispersing agent are used so long as the product obtained
is an aqueous dispersion of tetrafluoroethylene polymer. Typically, however, the
10 initiator will be a water-soluble peroxy compound such as an inorganic persulfate,
e.g. ammonium persulfate, or an organic peroxide, e.g. disuccinic acid peroxide, and
the dispersing agent used during polymerization will be an anionic dispersing agent
which imparts a negative charge to the polymer particles in the dispersion. The most
used anionic dispersing agents are the fluorinated carboxylic acid or carboxylates, e.g.
15 an ammonium polyfluorocarboxylate containing from 7 to 10 carbon atoms. The
amount of dispersing agent usually used is from 0.2 to 0.8 percent based on the weight
of polymer solids. The dispersion may be used in the present invention in this form
or may be concentrated to higher solids contents such as up to 75 percent by weight
polymer solids. Preferably, the particle size of the tetrafluoroethylene polymer particles
20 in the dispersion are of the larger size variety, i.e. at least 0.3 micron in average particle
diameter which can be made by the process of the aforementioned Punderson patent
by gradually adding the dispersion agent to the polymerisation system during the
early stage of polymerisation. The particles can be spherical or irregular in shape, for
example elongated. Particle size is determined by the light scattering method dis-
25 closed in the Punderson patent, except that the refractive index increment is taken
as 0.020 because of the presence of surfactant.

With respect to the melt-fabricable tetrafluoroethylene copolymer component of
the composition of this invention, the polymer thereof is a copolymer of tetrafluoro-
ethylene with at least sufficient other ethylenically unsaturated copolymerisable mono-
30 mer to render the resultant polymer melt fabricable. "Melt fabricable" means that the
copolymer has a specific melt viscosity of less than 10^7 poises at 380°C . at a shear
stress of 6.5 psi; conversely, "non-melt-fabricable" means that the polymer has a
specific melt viscosity of 10^7 poises or more at 380°C . at a shear stress of 6.5 psi.
Any other monomer which has the effect of making the resulting copolymer melt-
35 fabricable when copolymerised with tetrafluoroethylene can be used. Usually, no
more than 35 percent by weight of the copolymer will be formed from such other
monomer or monomers. Examples of such copolymers include the tetrafluoroethylene/
hexafluoropropylene copolymers disclosed in U.S. Patent Specification No. 2,946,763
(Bro and Sandt), the copolymers of tetrafluoroethylene with higher perfluoroalkenes
40 such as those containing from 4 to 10 carbon atoms, copolymers of tetrafluoroethylene
with perfluoro(alkyl vinyl ethers), e.g., perfluoro(propyl or ethyl vinyl ethers) disclosed
in U.S. Patent Specification No. 3,132,123 (Harris & McCane), and the copolymer
of tetrafluoroethylene with perfluoro(2-methylene-4-methyl-1,3-dioxolane) disclosed in
U.S. Patent Specification No. 3,308,107 (Selman and Squire), and the copolymers
45 of tetrafluoroethylene with highly fluorinated monomers, i.e. in which a single hydrogen
substituent remains which does not change the fluorocarbon character of the polymer,
such monomers being 2-hydroperfluoroalkene containing 3 to 10 carbon atoms, e.g.,
2-hydropentafluoropropene, the *omega*-hydroperfluoroalkenes from 3 to 10 carbon
atoms, and the *omega*-hydroperfluoroalkyl perfluorovinyl ethers in which the alkyl
50 group contains from 1 to 5 carbon atoms.

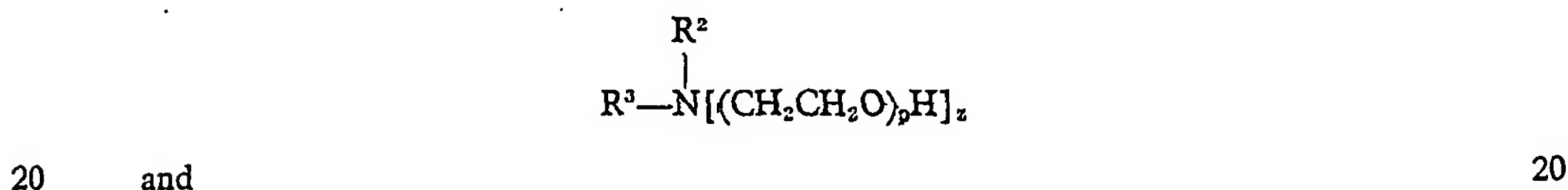
Aqueous dispersions of the above-described copolymers can be prepared substan-
tially in the same way as the tetrafluoroethylene polymer aqueous dispersions referred
to above. For example, the procedure of Example 1 of U.S. Patent Specification No.
2,946,763 (Bro and Sandt) can be followed.

55 The surfactant component of composition of the present invention is any nonionic
surfactant which is soluble in water at room temperature ($20-25^\circ\text{C}$.) at the concen-
tration desired. The nonionic surfactant can be composed of a single surfactant or a
mixture of nonionic surfactants. The nonionic surfactant preferably should have
sufficient volatility so that at least 95 percent by weight of the surfactant is burned
60 out of the tetrafluoroethylene polymer during its sintering which is generally done at
a temperature in the range of 340 to 400°C . for 5 seconds to 10 minutes. Typically
such surfactants are prepared as reaction products of ethylene oxide with such other
compounds which impart hydrophobic moieties to the resultant surfactant, e.g. propy-
lene oxide, amines, saturated and unsaturated alcohols and acids, and alkyl phenols.
65 Other suitable nonionic surfactants which do not involve reaction with ethylene oxide

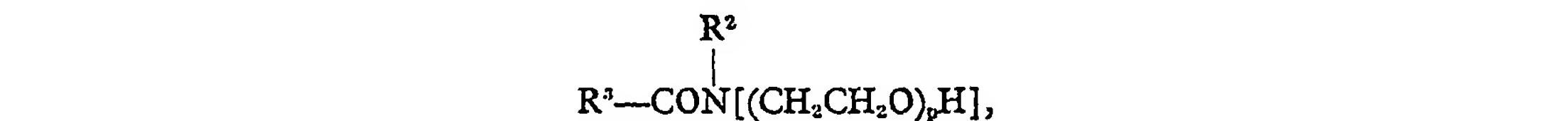
but which can be used in the present invention are the alkanol amides and fatty esters, such as the methyl esters of caprylic, caproic, stearic, and oleic acids. For purposes of illustration, some of the foregoing mentioned non-ionic surfactants are further illustrated hereinafter by the formulae:



wherein (A)_n is the group $-(C_2H_4O)_n-$ or a mixture of the groups $-(C_2H_4O)_a-$ and $-(C_3H_6O)_b-$, wherein n in each instance is an integer of from 2 to 50 and preferably 2 to 18, b is 0 or an integer of up to 30, and a is an integer of at least 2, (a+b) is equal to n; x is 1, 2 or 3; and R is an aliphatic hydrocarbon group which can be saturated or unsaturated, straight-chain, branched, or cyclic, and will generally contain from 8 to 24 carbon atoms, preferably from 8 to 18 carbon atoms; examples of R groups include oleyl, stearyl, tridecyl, lauryl, decyl and the groups derived from aliphatic glycols and triols; R'—C₆H₄O(B)_mH, wherein (B)_m is the group $-(C_2H_4O)_m-$ or a mixture of the groups $-(C_2H_4O)_c-$ and $-(C_3H_6O)_d-$, wherein m in each instance is an integer of from 2 to 50 and preferably 8 to 20, d is 0 or an integer of up to 30, c is an integer of at least 2, (c+d) is equal to m; R' is a monovalent aliphatic and usually saturated and containing 4 to 20 carbon atoms and preferably 8 to 12 carbon atoms;



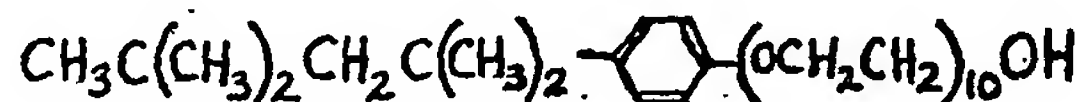
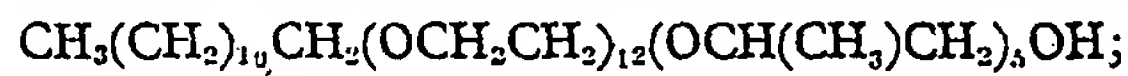
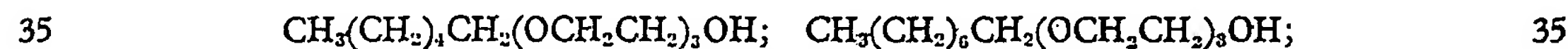
and



wherein p is an integer of 2 to 50, z is 1 or 2, R³ is an alkyl group containing 1 to 8 carbon atoms, R² is absent when z is 2 and an alkyl group of 1 to 8 carbon atoms when z is 1, with the proviso that at least 5 carbon atoms are provided by R³ when z=2 and by R² plus R³ when z=1; the polyalkylene oxide block copolymers of the formula:



wherein f is an integer of from 15 to 65 and e and g are integers sufficiently large that the total (C₂H₄O) groups represent 20 to 90 percent of the total weight of the polymer. For each of the surfactants of the foregoing described formulae, the hydrophobic and hydrophilic moieties are to be present in such proportions and the molecular weight of the surfactant is such that the aforementioned requirement of water solubility is met and preferably that the aforementioned degree of volatility is also met. Other specific surfactants which may be used include



The proportions of the components used to make compositions of the present invention will depend on the result desired. Only small amounts of the melt-fabricable copolymer and the dispersing agent are required to enhance the surface gloss of the tetrafluoroethylene polymer coating, and excessive amounts tend to detract from the beneficial properties of the tetrafluoroethylene polymer coating obtained. The composition accordingly contains 1 to 6 percent by weight of melt-fabricable copolymer based on the weight of tetrafluoroethylene polymer (a) present in the coating composition. The amount of nonionic surfactant will generally be from 3 to 15 percent

based on the total weight of polymer solids (tetrafluoroethylene polymer (a) and copolymer (b)) present in the composition, with the preferred range being from 4 to 9 percent by weight. The proportion of polymer solids in the composition is preferably from 40 to 65 percent based on the total weight of the composition.

5 The compositions of the present invention can be prepared by blending separate aqueous dispersions of the tetrafluoroethylene polymer (a) and copolymer (b). The surfactant may be dissolved in either of the dispersions or in the resultant blend thereof. The blending step is generally done with mild agitation so as to avoid coagulation of the aqueous dispersions and/or the resultant blend thereof. Further details on blending dispersions of this type for the purpose of preparing colloidal blends of a tetrafluoroethylene polymer with a tetrafluoroethylene/hexafluoroethylene copolymer is disclosed in U.S. Patent Specification No. 3,051,683 (Mallouk).

10 The compositions of the present invention may be cast in a conventional manner by contacting a substrate and the composition, followed by drying and sintering of the tetrafluoroethylene polymer (a) to give a polymer coating of improved gloss. The contacting step can take the form of spraying the dispersion onto the substrate or dipping the substrate into the dispersion to coat and/or impregnate the substrate. If the substrate is smooth surfaced, the coating can be removed to form film. The coating (or film) thickness can be built-up by repeated coating after each drying and sintering cycle.

20 The following Examples illustrate the present invention; (parts and percents are by weight unless otherwise indicated):

25 PREPARATION OF COMPOSITION — The co-dispersions were prepared by blending an aqueous dispersion of polytetrafluoroethylene (polymer (a)) with an aqueous dispersion of copolymer (copolymer (b)) under mild agitation to avoid coagulation. The nonionic surfactant was added neat, or as an aqueous solution, to the dispersions. The polymer solids concentration in the resultant dispersion was 49 percent based on the total weight of the dispersion.

30 MEASUREMENT OF GLOSS — Glass fabric (#128 type) was coated with various dispersion formulations according to the procedure described below. A swatch of cloth, 5-1/2" x 5", preferably coated with cement on all four edges to keep the cloth from unravelling, was clamped on opposite sides to a stretching apparatus. The apparatus was adjusted so that the cloth was taut. The stretched cloth was then dipped into the dispersion being tested for 15 seconds. After removal from the dispersion, the cloth was allowed to dry for 30 minutes at room temperature. This was followed by heating at 100°C. for 5 minutes and at 380°C. for four minutes. The cloth was flat and held its shape. Successive coats (either 5 or 6) were made in the same manner except the cloth was simply held by one 2-1/2" wide spring-loaded jaw clip. After the final coat, the coated cloth sample was trimmed to dimensions of about 4 x 4". The gloss of the square 4 x 4" sample was measured using a Portable Gardner 60° Glossmeter, Model GC-9045 (P-5), according to the procedure described below. The instrument was standardised first. It was placed on the surface of a primary black gloss standard, which had been cleaned, in a manner such that the light exiting the aperture was focused directly on the centre of the plaque. The glossmeter was turned on and allowed to warm up for at least 30 minutes. The rheostat knob was then adjusted until the meter read 94%. In a similar manner, the glossmeter was adjusted to 30 ± 1% using a secondary white standard. This calibration was checked occasionally during gloss reading determinations. The coated cloth sample was then placed on a 4-1/2" x 4-1/2" x 1/2" wooden plaque previously painted with flat black paint. After positioning the sample so that the edges were parallel with those of the plaque, the glossmeter was placed on the sample in such a manner that (1) the light exiting the aperture was focused directly on the centre of the sample and (2) the direction of the horizontal component of the light beam was parallel to an edge of the sample. At the end of a few seconds, the reading from the glossmeter was recorded. Two more readings were taken after the glossmeter had been moved successively to slightly different positions. Further series of three readings were obtained in the horizontal direction perpendicular to the above horizontal direction; similar series were taken on the other side of the coated glass cloth in the mutually perpendicular directions defined by the edges of the cloth. The overall average was taken as the gloss reading. Usually, the average of the readings in different directions was within ± 1 unit on the glossmeter scale.

EXAMPLE 1

In this Example, the tetrafluoroethylene polymer (a) aqueous dispersion contained 60 percent polytetrafluoroethylene solids based on the total weight of the dis-

persion, 6 percent of polyethylene glycol mono-para-octylphenyl ether, available as "Triton" X-100, based on the weight of polymer and had an average particle diameter of 0.23 micron. The coating of polytetrafluoroethylene on glass fabric, prepared by the previously described general procedure gave a glossmeter reading of 6 for seven coats having a total thickness of 9.7 microns.

A blend of this dispersion was prepared with 3 percent of "Triton" X-100 (based on the weight of the polytetrafluoroethylene in the dispersion) and 3 percent by volume based on the total volume of the co-dispersion of an aqueous dispersion of a tetrafluoroethylene/hexafluoropropylene copolymer containing 55 percent copolymer solids by weight, having an average particle diameter of 0.16 micron, and containing 6 percent "Triton" X-100 nonionic surfactant (based on the weight of the copolymer (b)) and having an infrared ratio of 3.49 ($A_{10.18\mu}/A_{4.25\mu}$) as measured by the procedure disclosed in U.S. Patent Specification No. 2,946,763 (Bro and Sandt) and a specific melt viscosity of $6-10 \times 10^4$ poises at 380°C . at a shear stress of 6.5 psi.

The total surfactant content was about 9 percent based on the total weight of polymer solids. Water was added to reduce the polymer solids content to 49 percent. The coating of the polymer blend for this co-dispersion on glass fabric, prepared by the previously described general procedure gave a glossmeter reading of 15 for seven coats having a total thickness of 9.4 microns.

This experiment was repeated except that the polytetrafluoroethylene in the polytetrafluoroethylene aqueous dispersion had a standard specific gravity (SSG) of 2.23 as compared to 2.22 for the polytetrafluoroethylene in the dispersion used earlier in this Example. The polytetrafluoroethylene aqueous dispersion by itself gave a glossmeter reading for the coating of 8 for seven coats having a total thickness of 9.5 microns. The composition consisting of this dispersion and the copolymer (b) dispersion (2 percent by volume) and surfactant gave a glossmeter reading for the coating of 20 for seven coats having a total thickness of 9.6 microns.

EXAMPLE 2

The procedure of Example 1 was repeated except that (a) the tetrafluoroethylene polymer (a) of the aqueous dispersion was replaced by a copolymer of tetrafluoroethylene and hexafluoropropylene as described in U.S. Patent Specification No. 3,142,665 (Cardinal, Edens, and Van Dyk) having an infrared ratio of 0.39 ($A_{10.18\mu}/A_{10.7\mu}$) and an average particle diameter of 0.18 micron (using a refractive index increment of 0.020 gms/cc), and (b) the total concentration of "Triton" X-100 was 8 percent based on the weight of total polymer solids. The composition of the co-dispersion plus surfactant gave a glossmeter reading of 18 for the coating of seven coats having a total thickness of 9.2 microns. The aqueous dispersion of this Example gave a glossmeter reading of 7 for the coating of seven coats having a total thickness of 10.1 microns.

EXAMPLE 3

The procedure of Example 1 was repeated except that the copolymer of the copolymer (b) aqueous dispersion was tetrafluoroethylene/perfluoro(propyl vinyl ether) copolymer having an infrared ratio of 2.80 ($A_{10.07\mu}/A_{42.25\mu}$) and a specific melt viscosity of about 140×10^4 poises at 380°C . at a shear stress of 6.5 psi. The dispersion of this copolymer was 60 percent polymer base solids based on the weight of the dispersion and contained 6 percent "Triton" X-100 based on the weight of the copolymer (no extra "Triton" X-100 was added to the co-dispersion). The composition comprising tetrafluoroethylene polymer (a) aqueous dispersion, copolymer (b) aqueous dispersion, and nonionic surfactant in the proportions set forth in Example 1 except as otherwise indicated herein gave a glossmeter reading of 12 on the coating comprised of 7 coats of a total thickness of 9.2 microns, as compared to a glossmeter reading of 6 for the coating prepared from polytetrafluoroethylene aqueous dispersion by itself.

EXAMPLE 4

The procedure of Example 1 was repeated except that the surfactant was a mixture of



and



wherein x, y and z are 10—11, 12—13, and 4—5, respectively, available as "Alfonic" 1012—60 and DN—65, respectively, the former being present in the amount 1.8 per-

cent and the latter 7.3 percent (by weight), based on the total weight of polymer solids (60 percent by weight) in the polytetrafluoroethylene dispersion. The codispersion-surfactant composition (no extra surfactant added to co-dispersion) gave a glossmeter reading of 17 for the coating comprising seven coats having a total thickness of 9.6 microns, as compared to a glossmeter reading of 6 for coating prepared from the polytetrafluoroethylene aqueous dispersion alone. The average particle diameter of the polytetrafluoroethylene in this Example was 0.34 micron.

The terms "TRITON" and "ALFONIC" as used in this specification are Registered Trade Marks.

10 WHAT WE CLAIM IS:—

1. A coating composition which comprises an aqueous dispersion of:
(a) a non-melt-fabricable (as hereinbefore defined) tetrafluoroethylene polymer,
(b) 1 to 6% by weight, based on the weight of (a), of a melt-fabricable (as hereinbefore defined) tetrafluoroethylene copolymer, and containing, dissolved therein, a non-ionic surfactant.

2. A composition according to claim 1 wherein the tetrafluoroethylene polymer (a) has an average particle diameter of at least 0.3 micron.

3. A composition according to claim 1 or 2 wherein the proportion of solids of tetrafluoroethylene polymer (a) and copolymer (b) is from 40 to 65% by weight, based on the total weight of the composition.

4. A composition according to any one of claims 1 to 3 wherein the proportion of nonionic surfactant is from 4 to 9% by weight, based on the total weight of the composition.

5. A coating composition according to claim 1 substantially as hereinbefore described.

6. A process for forming a coating on a substrate which comprises applying to the substrate a composition as claimed in any one of claims 1 to 5, drying the composition and sintering the tetrafluoroethylene polymer (a).

7. A process for forming a coating on a substrate according to claim 6 substantially as hereinbefore described.

8. Coated articles whenever prepared by a process as claimed in claim 6 or 7.

9. A process for preparing a film which comprises coating a smooth surfaced substrate by a process claimed in claim 6 or 7 and then removing the coating.

10. A process according to claim 9 substantially as hereinbefore described.

11. Film whenever prepared by a process as claimed in claim 9 or 10.

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